

METHODOLOGY TO DETERMINE SOLUBLE CONTENT IN DRY GRIND ETHANOL COPRODUCT STREAMS

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ABSTRACT. Distillers grains and syrup are coproducts from fuel ethanol dry grind processing. Ethanol manufacturing is dramatically increasing in the United States, primarily in Midwestern states, and thus the availability of these feed products is also growing. Confusion currently exists in industrial nomenclature regarding "solubles" in these streams because no standards are in place. In our study, dissolved materials were considered soluble matter. We developed a methodology to determine the dry basis soluble content in condensed distillers solubles (CDS) and distillers dried grains with solubles (DDGS). A mass balance analytical approach was initially used, but results were not in good agreement with experimental data. This method was thus deemed a poor predictor of final soluble content. This led to the development of a new methodology for determining, as well as predicting, soluble content for various coproduct streams, which produced results with $R^2 > 0.96$. This approach is applicable for all dry grind ethanol coproduct streams and is useful for value-added product development research.

Keywords. CDS, Coproducts, Corn, DDGS, Distillers grains, Ethanol, Solubles, Syrup.

Currently corn grain is the primary biological material that can be economically converted into fuel ethanol on an industrial scale. The corn-based ethanol industry is poised to produce substantial quantities of biofuel during the coming century as this industry continues its rapid expansion. The number of corn ethanol plants, and their processing capacities, has been markedly increasing in recent years. For example in 2005, 97 manufacturing plants in the United States had an aggregate production capacity of nearly 15.8 billion L/y (4.2 billion gal/y). More information on the historical growth of this industry can be found in Lyons (2003), BBI (2006), and RFA (2006).

Ethanol manufacturing from corn grain results in three main products: ethanol, the primary end product; residual nonfermentable corn kernel components; and carbon dioxide. In-depth information on ethanol processing can be found in Dien et al. (2003), Jaques et al. (2003), Maisch (2003), Tibelius (1996), and Weigel et al. (1997), but is beyond the scope of this article. The manufacture of fuel ethanol requires the carbohydrate portion of the grain; the other materials

(e.g., protein, fiber, oil), which are nonfermentable are superfluous to the process and are included in various coproduct streams. Following fermentation, the nonfermentable residual materials are removed from the process stream during the distillation stage as whole stillage. Excess water is removed via centrifugation; this thin stillage is then processed through evaporators to produce condensed distillers solubles (CDS). The solids removed from the centrifuge, known as distillers wet grains (DWG), are then combined with condensed distillers solubles, dried, and then sold as distillers dried grains with solubles (DDGS) for livestock feed. If the DWG is not combined with CDS during drying, the resulting product is known as distillers dried grains (DDG).

The sale of these coproducts contributes substantially to the economic viability of ethanol manufacturing and is thus a vital component to each plant's operations. Hence their nutritional content, quality, and consistency are important to ethanol processors. Several studies have examined chemical and nutritional properties of these byproduct feeds, including Belyea et al. (1998, 2004), Shurson et al. (2004), and Spiehs et al. (2002). Rosentrater et al. (2005) comprehensively reviewed much of the chemical and nutritional research to date.

CDS is commonly referred to as "syrup." CDS is generally a golden-brown, free-flowing to semi-solid fluid. It is an excellent source of vitamins, is low in fiber, relatively high in fat, and yields a digestible energy value approximately 91% of that of raw corn (Buchheit, 2002; Cruz et al., 2005). It typically contains approximately 28% to 46% dry matter, 6% to 21% (d.b.) fat, 18% to 22% (d.b.) protein, and 9% to 12% (d.b.) minerals (Belyea et al., 1998; Schingoethe, 2001). CDS is usually mixed with DWG at the ethanol plant and is then fed to livestock either in wet (DWGS) or dry (DDGS) form, both of which contain a high concentration of nutrients.

Increasing the CDS content in these combined coproduct streams alters subsequent properties (e.g., allowable storage time, angle of internal friction, angle of repose, bulk density,

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etc.) because of the addition of fat, protein, and other constituents. Quantification of these properties is important, as they affect storage and flow behavior, as well as potential end uses and value-added processing operations. CDS contains chemical constituents in both soluble and insoluble form. Unfortunately, there is currently confusion in the industry regarding what specifically constitutes “soluble” material. Additionally, there is often confusion regarding the assumption that all CDS solids are soluble. They are not, however, the same. The term “soluble” refers to a substance which is dissolved in a liquid. In other words, it is in solution, is present as a single phase, and cannot be physically removed without a phase change (Davis and Cornwell, 1991). Suspended materials, on the other hand, can be physically removed via filtration, centrifugation, or settling. With CDS there is potential for high fat content; this “fat” is actually corn oil that may be present as emulsified droplets. Moreover, soluble (dissolved) materials have been defined as the portion that pass through a filter under specified conditions, while insoluble (suspended) materials are the portion retained on the filter (Clesceri et al., 1998). In the industry there is currently no standard method employed for determining soluble content in the various dry grind ethanol residue streams. A robust methodology is therefore important for product development vis-à-vis specific soluble levels.

Currently, the goal of most dry grind facilities is to utilize the CDS by adding it to WDG during drying to produce DDGS. Often this is an inconsistent process with varying levels of soluble addition; this leads to variations in processing conditions and final nutrient levels. Therefore, the main objective of this study was to develop a methodology that can be readily used to determine soluble content in dry grind ethanol coproduct streams, so that DDGS with specific levels of solubles can be formulated. This type of methodology would be useful for both laboratory-scale product development and commercial-scale ethanol production when formulating DDGS.

MATERIALS AND METHODS

In our study, dissolved material was considered “soluble,” whereas suspended material was considered “insoluble.” Solubles in this study were thus the nonwater portion of a coproduct stream that passed through a filter media, while insolubles were the nonwater portion retained on the filter.

EXPERIMENTAL

Samples of CDS and DDG were obtained from a dry grind ethanol plant and were stored in sealed plastic buckets (the DDG at room temperature and the CDS at $4^{\circ}\text{C} \pm 1^{\circ}\text{C}$) until needed. To experimentally determine dry basis soluble content of each stream, 0.50 g of a specific coproduct material (e.g., CDS or DDG) was measured using a laboratory balance (Delta PM2500, Mettler, Hightstown, N.J.), placed in a centrifuge tube with 1.50-g distilled water, and then centrifuged (Model K, International Equipment Company, Needham Heights, Mass.) at 1700 rpm ($720 \times g$) for 10 min. After centrifugation, the sample was gravity filtered in a funnel and conical flask using Whatman 42 filter paper, which has a pore size of $2.5 \mu\text{m}$. This modification to the method of Clesceri et al. (1998) was utilized to allow a maximum quantity of solubles to pass, and was based upon

our preliminary investigations. After filtration, both the flask and the filter paper were placed in a laboratory oven at 135°C for 2 h (AACC 44-19, 1995) to evaporate all moisture present. Dry basis soluble content was then calculated as:

$$\text{Soluble \% (db)} = \frac{W_{\text{fl}}}{W_{\text{fl}} + W_{\text{fp}}} \times 100 \quad (1)$$

where W_{fl} was the mass of the dried matter (i.e., dissolved materials) in the flask (g), and W_{fp} was the mass of the dried matter (i.e., suspended materials) in the filter paper (g). All tests were conducted in triplicate. Statistical analyses on all collected data were then performed via Microsoft Excel v. 2003 (Microsoft Corp., Redmond, Wash.) software.

MASS BALANCE FOR DDGS FORMULATION

Ultimately, the goal of developing a methodology that can be used to determine dry basis soluble content in dry grind ethanol coproduct streams is essential to formulating DDGS with specific levels of solubles. This methodology will allow DDGS to be formulated at plants on a more scientific basis, instead of the methods of addition that are currently used. To prepare DDGS with specific dry basis soluble contents, appropriate proportions of CDS and DDG required for mixing must be determined. A dry basis, mass balance approach was initially used to accomplish this. According to calculated values, several batches of DDGS were prepared. Soluble levels were then measured using the aforementioned experimental method to determine the actual resultant dry basis soluble level in each batch. Experimental results were compared to the target levels used in the mass balance calculations to verify the methodology. Unfortunately, none of the DDGS batches achieved the target levels; a different approach was then used to produce DDGS with specific dry basis soluble contents.

CALIBRATION FOR DDGS FORMULATION

To develop an appropriate calibration for DDGS soluble content, various quantities of CDS (0.00 to 1.75 g, in intervals of 0.25 g) were thoroughly mixed with 0.50 g of DDG for 5 min. This range of CDS/DDG ratios (0 to 3.5) is likely to encompass those found in industrial practice. Immediately after mixing, distilled water was added and these samples were measured for solubles using the aforementioned experimental method, to determine the actual resultant dry basis soluble level in each. This empirical approach produced a direct quantification of dry basis soluble content, and although more time was required for sample preparation, this method alleviated the errors introduced via the mass balance calculation. Two separate batches of CDS and DDG were used to develop independent calibration curves. All CDS/DDG combinations were prepared and analyzed in triplicate for each batch.

RESULTS AND DISCUSSION

EXPERIMENTAL

As shown in table 1, it was determined using experimental measurements that the DDG in this study had residual solubles present. Instead of a negligible soluble content, the DDG actually contained 10.30% (d.b.). Thus, this DDG was, in reality, DDGS with a relatively low level of solubles.

Table 1. Resulting soluble contents (% , d.b.) for CDS and DDGS calibrations.

Coproduct	CDS (g)	CDS/DDG Ratio	Batch 1 ^[a]		Batch 2 ^[a]		Validation	
			Mean	SE	Mean	SE	Batch 3 ^[a]	
CDS	0.50	–	70.03	1.58	64.11	1.02	57.57	0.93
DDG (0.5 g)	0.00	0.00	10.30	0.37	10.30	0.37	10.83	0.26
	0.25	0.50	16.56	0.35	17.56	1.05	14.72	0.75
	0.50	1.00	22.19	0.77	21.91	0.54	18.44	0.46
	0.75	1.50	27.28	0.75	27.44	0.76	20.62	0.90
	1.00	2.00	30.89	0.68	30.26	0.42	24.09	0.86
	1.25	2.50	31.66	0.41	35.04	0.85	27.30	0.80
	1.50	3.00	34.28	0.33	36.45	0.68	30.41	0.52
	1.75	3.50	39.48	0.96	39.60	0.37	33.72	0.57

[a] Sample size of n = 3 was used for each batch of each CDS/DDG ratio.

Anecdotal, this is a fairly common level throughout the ethanol industry vis-à-vis DDG production. On the other hand, the CDS used in the study had a soluble content ranging from 64.11% to 70.03% (d.b.). These variations underscore the need to experimentally determine soluble content for each batch of interest, especially when attempting to formulate DDGS with specific soluble levels.

MASS BALANCE FOR DDGS FORMULATION

Prior to the development of a calibration procedure, a mass balance calculation method was used to determine the quantity of CDS (g) and DDG (g) that should be mixed to produce DDGS with a specific dry basis soluble content. To illustrate this approach, and using data from a preliminary experiment with an initial batch of CDS that contained a soluble content of 54.71% (d.b.) and a batch of DDG with a soluble content of 7.80% (d.b.), an example calculation and subsequent numerical results are provided below for obtaining DDGS with a target soluble level of 24.00% (d.b.). On a dry basis, a total mass balance (which includes soluble and insoluble materials) to produce 100.00 g of dry DDGS:

$$M_{DDG} + M_{CDS} = M_{DDGS} = 100.00 \quad (2)$$

where M denotes mass (on a dry matter basis). Considering only soluble solids (dry) mass balance:

$$M_{CDS} \times X_{CDS} + M_{DDG} \times X_{DDG} = M_{DDGS} \times X_{DDGS} \quad (3)$$

where X denotes soluble solids (on a dry matter basis), with $X_{CDS} = 54.71\%$ (d.b.); $X_{DDG} = 7.80\%$ (d.b.); $X_{DDGS} = 24.00\%$ (d.b.). Substituting these values into equation 3 produces:

$$54.71 \times M_{CDS} + 7.80 \times M_{DDG} = 24.00 \times M_{DDGS} \quad (4)$$

Using equation 2, and algebraically solving for M_{CDS} results in a value of 34.54 g. Substituting this calculated M_{CDS} value into equation 2 above produces a M_{DDG} value of 65.46 g.

According to these calculated quantities, DDGS with a target content of 24.00% soluble solids was prepared. After mixing appropriate quantities of CDS and DDG, the prepared samples were then analyzed for soluble content, to verify the validity of the mass balance approach. Results are provided in table 2. As shown, the DDGS prepared according to the quantities determined by the mass balance above produced soluble contents between 21.05% and 22.05% (d.b.), and did

not achieve the target level of 24.00%. Instead, the resulting soluble levels had between 8.14% and 12.30% error. There may have been binding (possibly adsorption or diffusion) or crystallization which occurred during the mixing process that caused the resulting levels of solubles to be lower than the target level. These sources of error were not, however, easily identifiable and were not pursued. A follow up study to investigate this speculation is in order. Thus, mass balance was deemed inappropriate for accurately producing DDGS with specific soluble contents, and the calibration strategy was employed instead.

CALIBRATION FOR DDGS FORMULATION

Results from the empirical calibrations for Batch 1 and 2 are provided in table 1; figure 1 shows regression curves that were developed. These curves, each of which had a coefficient of determination (R^2) greater than 0.96 and low standard error, fit the observed experimental data quite well, and can be used to determine the quantity of solubles which are present in the prepared DDGS. It is important to point out that the DDGS results are based upon mixing the denoted quantity of CDS (i.e., the x-axis) with 0.50 g of DDG. Developing appropriate scale-up factors will be essential when applying the developed calibration equations to larger quantities of DDGS (e.g., on a pilot or production scale).

To further validate this methodology, a third batch of CDS and DDG were analyzed. Data resulting from this trial are provided in table 1; figure 1 shows the calibration curve developed for the validation runs. Similar to the other batches, this curve also showed a high coefficient of determination (R^2 of 0.99) and little experimental error.

Soluble calibration, such as that developed here, can be used to determine the quantity of each coproduct stream that must be combined to produce DDGS with a specific level of

Table 2. Resulting DDGS soluble contents produced according to mass balance calculation for a target of 24% (d.b.) solubles, using CDS with a soluble content of 54.71% (d.b.) and DDG with a soluble content of 7.80% (d.b.).

Run	W _{fl} (g)	W _{fp} (g)	Soluble Content (% , db)	Error (%)
1	0.20	0.69	22.05	8.14
2	0.19	0.69	21.40	10.85
3	0.19	0.69	21.05	12.30

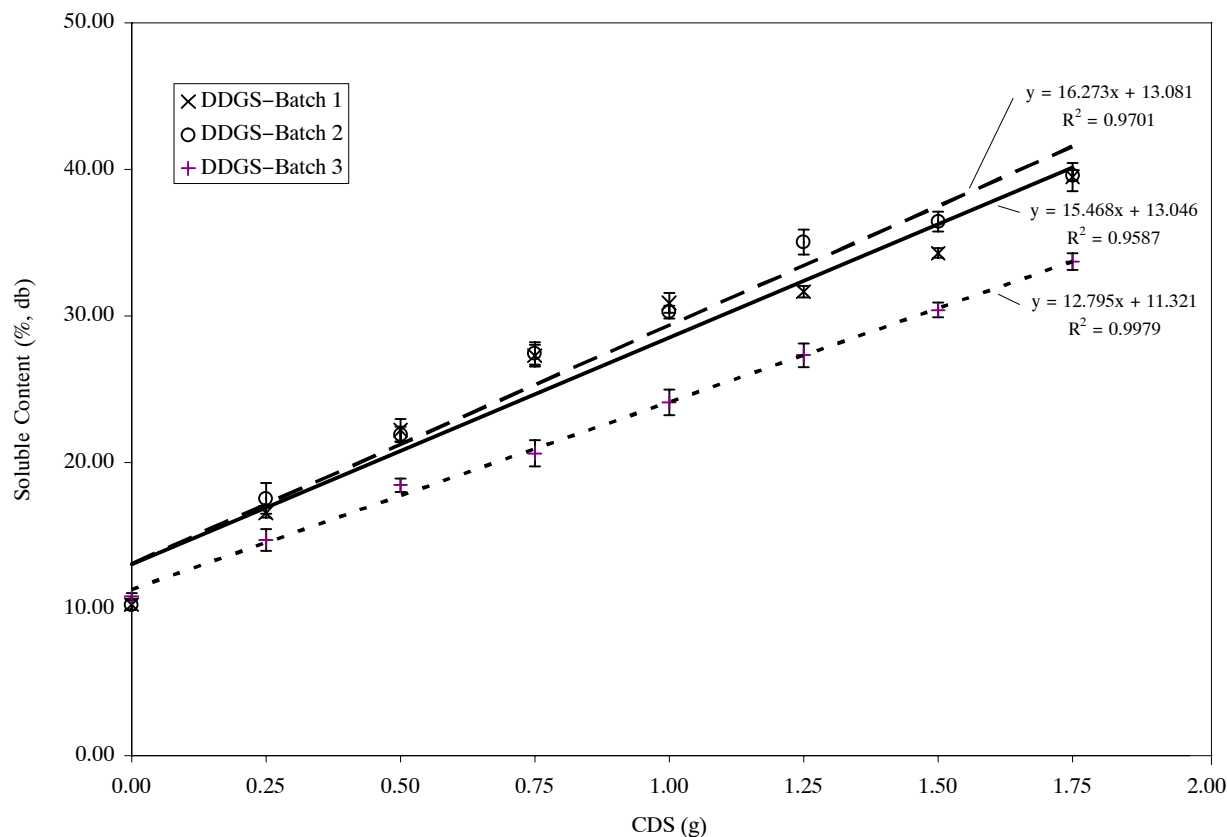


Figure 1. Calibration curves and data points (\pm S.E.) for determination of soluble content in DDGS formulated using 0.50 g of DDG.

solubles and will alleviate potential problems that may arise using a mass balance approach. Chemical analysis of the insoluble and soluble fractions is warranted and may give indication of whether chemical changes occur due to mixing, which give rise to mass balance inconsistencies. Because the soluble content of these residue streams differs between batches, operators, production plants, etc., though, the soluble levels in them will have to be determined for each batch of interest, and resulting calibration curves will have to be created for each, in order to produce DDGS with specific levels of solubles. The protocols described in this article can be used to accomplish this and will be utilized in a subsequent study to analyze these differences.

CONCLUSIONS

Soluble content plays a fundamental role in the chemical and physical properties of ethanol dry grind coproduct streams. Addition of CDS (especially the soluble materials within) to coproduct streams affects the composition as well as the resulting properties of DDGS. The goal of this article was to develop a methodology that can be readily used to determine soluble content in these coproduct streams, so that DDGS with specific levels of solubles can be formulated. Although mass balance did not work well, the calibrated approach developed here had very favorable results ($R^2 > 0.96$) and is applicable to both laboratory and production-scale settings. This article represents an initial step in an ongoing effort to add value to distillers grains and other dry grind ethanol residues. Future work will quantify how variations in soluble content lead to differences in subsequent

chemical and physical properties, including flowability, which is a major concern for the industry.

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